

PROTON MAGNETIC RESONANCE SPECTROMETRY
IN THE CHARACTERIZATION OF COAL-TAR PITCHES

C. W. DeWalt, Jr., and M. S. Morgan

Mellon Institute
Pittsburgh 13, Pennsylvania

Introduction

Coal-tar pitch is the residue, boiling at temperatures above 350° C, from the fractional distillation of coal tar. Although it constitutes about 50% of the tar yield from high-temperature carbonization in coke ovens, its chemical composition is not nearly as well known as that of many of the smaller, more-volatile fractions. Coal-tar pitch has numerous large-scale uses, some of which call for modification of the material by physical or chemical techniques. However, much of this modification is empirical to the extent that the results are measured in terms of efficacy for a specific end-use rather than in terms of change in chemical structure. Additional investigations of the chemistry of this rather intractable material are desirable toward developing new uses and placing pitch-treating procedures on a more scientific basis. With the development of proton magnetic resonance (PMR) techniques, a promising method of examining the types of hydrogen in pitches became available. Attention was therefore turned to the results which might be obtained by PMR examination of pitches.

Chemically speaking, pitch cannot be considered as a single type, but rather there are large differences between pitches, depending upon their source. Coke-oven pitches, which are of primary concern in this paper, are produced from high-rank (coking) coals at very high temperatures (1000° to 1300° C). The severe conditions control the product so that coke-oven pitches constitute a narrow class among coal-tar pitches, as indicated by Volkmann.¹ They are the most aromatic of the pitches, and a precise aromaticity determination is necessary to distinguish one from another.

The aromaticity of a pitch can be defined by two parameters. One is the ratio of the aromatic structures to the whole pitch. The other is the degree of condensation of the aromatic portion. This degree of condensation could range from the polyphenylene- to the graphite-type. Aromaticity factors can be calculated from various types of data, including density, atomic C/H ratio, and the ratio of aromatic hydrogen (Har) to total hydrogen (H). The latter is the most sensitive method for highly aromatic materials like coke-oven pitches, since the proportion of non-aromatic hydrogen atoms is greater than that of non-aromatic carbon atoms. For example, methyl-phenanthrene with 6.7% non-aromatic carbon atoms has 25% non-aromatic hydrogen atoms.

Considerable work has been reported toward establishing an infrared Har/H measurement,^{2,3,4,5,6} but more detailed and reliable data are reported from PMR measurements.^{2,6,7,8,9} Three types of hydrogen were estimated in pitch-like materials by PMR methods: aromatic hydrogen (Har); hydrogen on saturated carbon alpha to aromatic rings, or alpha hydrogen (H_α); and hydrogen on other saturated hydrocarbon structures, or beta hydrogen (H_β). Both Brown and Ladner² and Oth and Tschamler⁸ were able to calculate structural parameters for pitch-like materials through the use of such PMR data.

For structural analysis, Brown and Ladner's² method appeared especially suitable for adaptation to coke-oven pitch. Details of the structure of the aromatic portion of their pitch-like materials were derived by subtracting the non-aromatic atoms from the whole. This introduced an uncertainty by requiring an estimate of the H/C ratio in the substantial fraction of non-aromatic structures. Nevertheless, the parameters of their distillates proved to be functions of the ranks of the parent coals. Coke-oven pitches in this analysis should enjoy the advantage of a very low proportion of non-aromatic structures.

Rao, Murty, and Lahiri⁶ reported the use of the PMR spectrum in the characterization of the 65 weight per cent carbon disulfide-soluble fraction of a pitch that was evidently of coke-oven origin. Only 22% of the hydrogen was non-aromatic, and 70% of the non-aromatic hydrogen was of the alpha type. They concluded that the non-aromatic hydrogen was mostly present as methylene-, methyl-, and small alkyl-substituents on aromatic ring systems.

This paper describes the application of PMR spectrometric methods to the determination of certain aspects of the chemical structure of coke-oven pitches.

Experimental

A series of coke-oven pitches representing a wide range of electrode-binder properties with a narrow range of softening points and, for comparison purposes, a low-temperature-carbonization pitch from a sub-bituminous B coal were selected. The analytical data for these pitches, together with the sources and methods of preparation, are summarized in Table I.

A.C.S. reagent-grade carbon disulfide was used to prepare the pitch extracts for the PMR determinations. The internal PMR standard was Anderson Chemical Division of Stauffer Chemical Company's "pure" grade of tetramethylsilane (TMS). The reference compounds were fluorene, m.p. 114-116° C (lit., 115-116° C), and acenaphthene, m.p. 93-94° C (lit., 95° C).

Carbon Disulfide-Soluble Fractions of Pitches

The carbon disulfide-soluble PMR spectra samples were prepared in the following manner: Samples of the pitch weighing 5.00 g. and sized to pass a 20-mesh sieve were added to 50 ml. of carbon disulfide in a 250-ml. beaker with stirring. The beaker was covered with a watch glass, and the magnetic stirring was maintained for 30 minutes. After collecting the insolubles on a 60-ml., medium-porosity fritted-glass funnel and washing with 25 ml. of carbon disulfide, the solids were air-dried and weighed. The filtrate and washings were concentrated on the steam bath (in a hood) to give a 60% weight/volume (w/v) solution. Samples of this solution and of dilutions made up as needed were placed in Varian A-60 Spectrometer sample tubes, and a trace of TMS was dissolved in each sample.

Determination of PMR Spectra

The PMR spectra were recorded on a 10 in. by 20 in. record sheet using a Varian A-60 Spectrometer. The samples were spun rapidly at room temperature, and the spectra were traversed slowly (sweep time 500 sec.) from 550 to 50 cycles per second (c.p.s.) below the TMS line (the increasing-frequency convention was observed). Radio-frequency (RF) power settings were intermediate—between 0.04 and 0.20 milligauss (mG.)—and filter bandwidth was usually set at 1 c.p.s.

Determination of the Integrals of the PMR Spectra

After plotting a spectrum, the integral of the curve was recorded electronically in a 10 in. by 20 in. area of chart, using the same sample and conditions,

with the exceptions and precautions noted below (see Figure 1). Care was necessary to insure both stability of the integral and non-saturation of any of the sample protons. To avoid saturating sample protons, the RF energy was kept below a setting of about 0.4 mG., while the sweep time was set down to 50 or 100 seconds. Saturation of a particular proton would result in an area under its absorption band less than proportional to the number of protons represented. Three factors were used to obtain stable integrals. The use of only the most concentrated, the 30 and 60% w/v, solutions for integrals was important. Also, the sweep time was reduced to 50 or 100 seconds, and finally, it was sometimes advantageous to increase the RF power.

Estimation of Hydrogen Types from PMR Integrals

Quantitative estimation of the hydrogen types involved measurement of the integral heights at the following frequencies (tau values; see Figure 1): for aromatic hydrogen together with phenolic hydrogen (H_{ph}), approximately 4.5 tau; for alpha² hydrogen (H_{α²}; this is hydrogen on any carbon atom which joins two aromatic rings), 6.60 tau; for alpha hydrogen, approximately 8.1 tau; and for beta hydrogen, the end of the spectrum (about 9.2 tau). These boundary tau values were equivalent to the following frequencies in c.p.s. below TMS: about 4.5 tau, near 315 c.p.s.; 6.60 tau, 190 c.p.s. for 30% and 180 c.p.s. for 60% w/v solutions; and 8.1 tau, 110 c.p.s. for both 30 and 60% solutions. The considerations which led to the choice of these frequencies will be discussed in the following section.

PMR Frequencies (Tau Values)

The use of dissolved TMS eliminated volume susceptibility corrections¹⁰ and interference by the standard in regions where the pitch components absorbed. It did not, however, prevent anomalous aromatic medium effects¹¹ from interfering. The spectra of different concentrations of pitch fractions in carbon disulfide showed frequency differences as great as 0.40 p.p.m. (tau units). To eliminate these effects, extrapolation to infinite dilution with the internal standard was necessary. This procedure with CS₂ extracts of pitches 1 and 2 gave smooth curves and infinite dilution frequencies for various absorption components of the spectra (see Figure 2).

The use of carbon disulfide provided a pitch solvent with Van der Waals deshielding effect about the same as that of carbon tetrachloride,¹² the tau solvent. Therefore, the infinite dilution frequencies should be very nearly true tau values,¹³ in which form they are herewith reported. This was confirmed by the value of 6.68 tau thus obtained for the methylene line of acenaphthene in pitch (lit., 6.66 tau).

The choice of the frequencies listed in the preceding section to divide between the four types of hydrogen was made in the following manner: There was a broad region of zero signal between aromatic and non-aromatic bands, centering in the 4.5 tau region. The alpha² hydrogen, since it is close to two rather than one aromatic ring, is more deshielded than alpha hydrogen. Thus, the alpha² hydrogen absorption occurs at lower tau values (frequencies). The boundary was chosen just below the acenaphthene methylene peak at 6.66 tau because this is an intermediate type between alpha and alpha², although it is formally alpha hydrogen. Conservatively, then, absorption below 6.60 tau was attributed to alpha² hydrogen. The anomalous shifts due to changes in pitch concentration necessitated the use of the two frequencies. For the boundary between alpha and beta hydrogen, the spectrum of pitch 7, which showed separate absorption maxima for beta and for alpha hydrogen types, was considered (see Figure 3). The minimum between these maxima occurred at about 8.2 tau. To avoid overestimating alpha hydrogen, a value near 8.1 tau was chosen. This includes types such as durene methyl groups (7.86 tau) and excludes such types as Me₃CH (8.44 tau) and cyclohexane (8.56 tau).

Molecular Weight Determination

Molecular weight measurements were ebullioscopic with incremental addition of sample and extrapolation to infinite dilution. Solvents were benzene and freshly prepared chloroform, depending upon the solubility of the sample. Interference by foaming or incomplete solubility prevented determination of molecular weight in certain cases (see Table II).

Structural Parameters

From PMR and elementary analytical data, Brown and Ladner² were able to calculate the following average structural characteristics of their pitch-like materials:

f_a , the ratio of aromatic carbon (C_a) to total carbon (C),

σ , the fraction of the total available outer-edge positions of the aromatic skeleton which is occupied by substituents, and

H_{ar}/C_a , the atomic H/C ratio that the average aromatic skeleton would have if each substituent were replaced by a hydrogen atom.

Brown and Ladner developed the following equations for calculating these parameters:

$$f_a = \frac{\frac{C}{H} - \frac{H_\alpha^*}{x} - \frac{H_\beta^*}{y}}{\frac{C}{H}} \quad (1)$$

$$\sigma = \frac{\frac{H_\alpha^*}{x} + \frac{O}{H}}{\frac{H_\alpha^*}{x} + \frac{O}{H} + H_{ar}^*} \quad (2)$$

$$\frac{H_{ar}}{C_a} = \frac{\frac{H_\alpha^*}{x} + \frac{O}{H} + H_{ar}^*}{\frac{C}{H} - \frac{H_\alpha^*}{x} - \frac{H_\beta^*}{y}} \quad (3)$$

where C/H and O/H are the atomic ratios, obtained from elementary analysis; $H_\alpha^* = H_\alpha/H$, the ratio of alpha-type hydrogen to total hydrogen obtained from PMR spectrometric analysis; $H_\beta^* = H_\beta/H$, the ratio of beta-type hydrogen to total hydrogen from PMR analysis; $x = H_\alpha/C_\alpha$ and $y = H_\beta/C_\beta$, the atomic ratios of hydrogen to carbon in the alpha and beta structures, both of which must be obtained by estimate; $H_{ar}^* = H_{ar}/H$, the ratio of aromatic hydrogen to total hydrogen obtained indirectly from PMR spectrometry with the help of elementary analysis, assuming 60% of the total oxygen to be phenolic. Since phenolic hydrogen (H_{ph}) is included in the "aromatic" hydrogen ($H_{ar} + ph$) seen in PMR spectra, H_{ar}^* was calculated by the following equation:

$$\frac{(\text{Har} + \text{ph})}{\text{H}} - 0.60 \frac{\text{O}}{\text{H}} = \frac{\text{Har}}{\text{H}} = \text{Har}^*$$

They assumed that every oxygen atom was present as a substituent on an aromatic nucleus in completing the development of the above equations.

Their method for the conversion of the hydrogen distribution in coal-like materials to carbon structure was adapted for use with coke-oven pitches. Changes were made in the assumptions and equations as described below. It is accepted that 60% of the total oxygen is phenolic, but Brown and Ladner's assumption that all of the oxygen occurred as substituents on aromatic nuclei could not be justified for coke-oven pitches. Instead, the remaining 40% oxygen is assumed to occur not as aromatic substituents but in other forms, among which heterocyclic oxygen must be included. Alpha² hydrogen is included in the equations separately as $\text{H}\alpha^2$, with $z = 2$ the estimated ratio of hydrogen to carbon in such groups, and $\text{H}\alpha^{2*} = \text{H}\alpha^2/\text{H}$. Because the predominant alkyl substituent in known coke-oven pitch components is the methyl group, the value of x (estimated H/C ratio for alpha structures) is raised from the value of 2 to 2.5. The value of $y = 2$ is retained.

Considering equation (1), a term for alpha²-type carbon is added to its numerator, the number of aromatic carbon atoms, giving $\text{C} - \text{C}\alpha^2 - \text{C}\alpha - \text{C}\beta$. The resulting equation for coke-oven pitches is the following:

$$f_a = \frac{\frac{\text{C}}{\text{H}} - \frac{\text{H}\alpha^{2*}}{2} - \frac{\text{H}\alpha^*}{2.5} - \frac{\text{H}\beta^*}{2}}{\frac{\text{C}}{\text{H}}} \quad (4)$$

Considering equation (2), it is necessary to add a term for the contribution of alpha² structures to the total number of substituents. Since each bridge represents two substituents, this added term must equal $2 \times \text{C}\alpha^2$, which is $2 \text{H}\alpha^2/z$. To replace (2) for determining the degree of substitution of coke-oven pitches, the following equation is used:

$$\sigma = \frac{\text{H}\alpha^{2*} + \frac{\text{H}\alpha^*}{2.5} + 0.6 \frac{\text{O}}{\text{H}}}{\text{H}\alpha^{2*} + \frac{\text{H}\alpha^*}{2.5} + (\text{Har} + \text{ph})^*} \quad (5)$$

Similarly, equation (3) is replaced by the following equation for the atomic C/H ratio of the hypothetical unsubstituted average aromatic nucleus of coke-oven pitches:

$$\frac{\text{Car}}{\text{Haru}} = \frac{\frac{\text{C}}{\text{H}} - \frac{\text{H}\alpha^{2*}}{2} - \frac{\text{H}\alpha^*}{2.5} - \frac{\text{H}\beta^*}{2}}{\text{H}\alpha^{2*} + \frac{\text{H}\alpha^*}{2.5} + (\text{Har} + \text{ph})^*} \quad (6)$$

This degree-of-condensation parameter is also the ratio of total aromatic carbon to aromatic edge-carbon.

Equations 4, 5, and 6 were used to calculate parameters for the carbon disulfide solubles of eight pitches and for the carbon disulfide-soluble, n-hexane-insoluble (resin) fraction of one of the coke-oven pitches. The parameters of low-temperature-carbonization pitch 7 were calculated by means of equations 1, 2, and 3. Data and results are listed in Table II.

Results and Discussion

PMR Spectra of Coke-Oven Pitches

The carbon disulfide-soluble fractions of coke-oven pitches, using the Varian A-60 Spectrometer, showed hydrogen distributions in keeping with the reputed high aromaticity of these pitches. From 80 to 90% of their hydrogen was aromatic. The higher molecular weight resin fraction of pitch 2 had an even higher (95%) aromatic hydrogen content. This is in sharp contrast with the 20% of aromatic hydrogen in the low-temperature-carbonization pitch carbon disulfide-soluble fraction.

There were only two absorption maxima in the coke-oven pitch spectra: the aromatic- and the alpha-hydrogen bands. Both indicate types closely associated with aromatic rings. Reports on other pitches^{2,3,8} have shown an additional band due to hydrogen not associated with any aromatic ring (beta hydrogen). Low-temperature-carbonization pitch 7 also fell in the latter category (see Figure 3), exhibiting two maxima in the beta hydrogen region. The total alpha and alpha² hydrogen in coke-oven pitches was never less than 79% of the non-aromatic hydrogen. Thus, only 21% of the non-aromatic and only 4.2% of the total hydrogen failed to show a close proximity to an aromatic ring.

In addition to the above considerations, which are based on tau values, there was the sensibility of the non-aromatic protons of the coke-oven pitches to the anomalous aromatic medium shifts. This is a further indication that these protons are held close to aromatic rings, since paraffins were insensitive to these effects.

Individual Components

Without fractionating the pitches, it was possible in four cases to identify acenaphthene, and in two, fluorene, as components of the pitch. There is a possibility that yet other of the more abundant components could thus be identified, since a number of sharp individual peaks appeared in each spectrum. Two factors combined to confirm the conclusions as to identity. The first factor was the identity of the peaks in question with those of the added authentic compound at one concentration. The second factor was repetition of the same results at another concentration of the pitch in the solvent. Thus, the aromatic medium effect was shown to be the same for the authentic compound and the pitch component.

Structural Parameters

A Brown-Ladner type of analysis of the PMR and elementary analytical data, together with molecular weight data, permitted the following conclusions regarding molecular structure (see Table II):

Carbon Aromaticity (fa)

The coke-oven-pitch carbon disulfide-soluble fractions were estimated to contain only 2.5 to 5.7% non-aromatic carbon atoms ($f_a = 0.975$ to 0.943). A contrast between coke-oven pitch 2 and low-temperature-carbonization pitch 7 is available through their resin fractions, which by calculation contained 1 and 33% non-aromatic carbon ($f_a = 0.987, 0.67$), respectively.

Degree of Substitution (σ)

Only from 6 to 12 of every 100 available sites for substitution around the average nucleus were occupied by substituents in these coke-oven-pitch fractions ($\sigma = 0.063$ to 0.116). The value was 2 per 100 lower ($\sigma = 0.048$) in the larger molecular weight fraction of pitch 2. Such trends to less substitution in larger

molecules of pitch have been reported by other workers using other methods.^{14,15} Again, comparison with pitch 7 serves to emphasize the high aromaticity of the coke-oven pitches. Sixty five per cent ($\sigma = 0.65$) of the edge aromatic carbons were bonded to substituents in pitch 7 resin fraction.

C/H of the Aromatic Nucleus (Car/Haru)

The atomic C/H ratios of the average hypothetical unsubstituted aromatic nucleus (Car/Haru values) of the coke-oven pitches were, for carbon disulfide-soluble fractions, 1.5 to 1.7, and for the resin fraction of pitch 2, 1.83 (Table II). The interpretation of these numbers depends upon the molecular weight of the materials. With the molecular weights, the degree of condensation of the average aromatic nucleus was shown to be nearly linear (of the benzene-naphthalene-phenanthrene series: each ring fusion involves only two carbon atoms).

The average molecular weight of the carbon disulfide-soluble fraction was about 400. As a result, an average aromatic nucleus of 7 to 8 rings with one substituent was indicated. The resin fraction of pitch 2 with molecular weight 660 would indicate an average aromatic nucleus with near 13 rings and about 1.3 substituents.

To illustrate this, for the fractions of pitch 2, a type molecule was chosen as a possible structure for the average molecule, as shown in Table III. This suggests that the higher molecular weight fractions of coke-oven pitch, such as the C-1 sooty material, do not approach graphite in structure but may be mostly linearly condensed aromatic ring systems.

PMR Solvent

Carbon disulfide proved to be a good solvent for PMR examination of coke-oven pitches. The soluble fraction represented a large proportion—60 to 84%—of the total material. Solutions of concentrations up to 60% were readily available in this non-protonic solvent, permitting accurate quantitative work, and the infinite dilution values were very nearly true tau values.

Summary

Proton magnetic resonance spectrometry proved a useful method for the characterization of coke-oven pitch. The estimation of aromatic and three types of aliphatic hydrogen by this means made possible the formulation of a structure for the typical molecule in the carbon disulfide-soluble fraction. This was a linearly condensed aromatic nucleus with 2 to 6% of the carbon atoms occurring as substituents which were predominantly methyl groups. The average molecular weight was near 400, which was equivalent to 7 or 8 fused aromatic rings. Fluorene and acenaphthene were identified in several of the pitches. It is hoped that these methods will prove to be of value in a search for correlations between the chemical and physical properties of a coke-oven pitch and its efficacy in a particular industrial end-use.

Acknowledgement

This work was done by the Coal Chemicals Research Project, sustained by the United States Steel Corporation, to whom the authors wish to express appreciation for permission to publish the results. The authors also wish to acknowledge their indebtedness to Dr. A. A. Bothner-By, Dr. B. L. Shapiro, and Mr. F. E. Dickson of the Mellon Institute for their assistance in obtaining and interpreting the PMR spectra.

References

- (1) E. W. Volkmann, "The Structure of Coke Oven Tar," Fuel, **38**, 445-468 (1959).

- (2) J. K. Brown and W. R. Ladner, "A Study of the Hydrogen Distribution in Coal-Like Materials by High-Resolution Nuclear Magnetic Resonance Spectroscopy. II," Fuel, 39, 87-96 (1960).
- (3) M. B. Dell, "Characterization of Pitches for Carbon Anodes," Fuel, 38, 183-187 (1959).
- (4) L. J. Wood and W. G. Wilman, "Chemical Nature of Coal Tar Pitch," Proceedings: Residential Conference on Science in the Use of Coal, Sheffield, Institute of Fuel, London, 1958, pp. C10-C14.
- (5) L. J. Wood, "Chemical Constitution of Road Tars and Coal-Tar Pitches," J. Appl. Chem., 11, 130-136 (1961).
- (6) H. S. Rao, G. S. Murty, and A. Lahiri, "The Infra-Red and High-Resolution Nuclear Magnetic Resonance Spectrum of Coal Tar Pitch," Fuel, 39, 263-266 (1960).
- (7) L. M. Jackman, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, Pergamon Press, New York City, 1959.
- (8) J. F. M. Oth and H. Tschamler, "Comparison and Interpretation of Proton Spin Resonance Measurements on a Coal Extract in the Solid State and in Solution," Fuel, 40, 119-122 (1961).
- (9) J. K. Brown, W. R. Ladner, and N. Sheppard, "A Study of the Hydrogen Distribution in Coal-Like Materials by High-Resolution Nuclear Magnetic Resonance Spectroscopy. I," Fuel, 39, 79-86 (1960).
- (10) L. M. Jackman, op. cit., pp. 41-48.
- (11) A. A. Bothner-By and R. E. Glick, "Medium Effects in the Nuclear Magnetic Resonance Spectra of Liquids. III. Aromatics," J. Chem. Phys., 26, 1651-1654 (1957).
- (12) A. A. Bothner-By, "Medium Effects in the Nuclear Magnetic Resonance Spectra of Liquids. IV. Nature of the Effects," J. Mol. Spectry., 5, 56 (1960).
- (13) See reference 7, page 47, for a definition of tau value.
- (14) H.-G. Franck, "The True Nature of Bituminous Coal Tar Pitch," Brennstoff-Chem., 36, 12-19 (1955).
- (15) C. Karr, Jr., J. R. Comberiata, and P. A. Estep, "Ring Analysis and the Spectral Characterization of Resins from Pitch of Low Temperature Tar," Fuel, 41, 167-176 (1962).

Table I

Analytical Data, Sources, and Methods of Preparing
Experimental Pitches

<u>Pitch Designation^{a)}</u>	<u>Softening Point, °C, C.I.A.^{b)}</u>	<u>Benzene Insoluble, Wt. %</u>	<u>Quinoline Insoluble, Wt. %</u>	<u>Atomic C/H Ratio</u>
1	89.0	33.2	13.1	1.80
2	90.2	32.6	12.8	1.93
3	93.5	29.7	10.58	1.87
4	94.9	28.0	9.13	1.76
5	90.6	17.5	6.87	1.78
6	88.2	13.0	2.44	1.61
A	102.3	25.5	12.4	1.84
C	95.0	25.0	4.2	1.73
7	59.5	—	—	0.95

- a) 1. Thermal treatment of a 74° C pitch at 380° C for 24 hours and back-blending with 9.1% of starting pitch. 2. Laboratory distillation of soft pitch from a production tar. 3. Laboratory distillation of 36.2 wt. % from a production tar. 4. Blend of 88.55 wt. % 105° C pitch (produced by distillation of light tar at 50 mm. to 300° C) with 11.45% of coal-tar distillate oil (boiling 230° to 270° C). 5. A production pitch after removal of n-heptane solubles. 6. Laboratory distillation of a 69° C pitch from light tar. A. Produced by plant distillation of production tar. C. Produced by adding quinoline to the parent tar of A, centrifuging this mixture to remove insolubles, and then distilling. 7. A 60° C pitch produced by blowing at 120° C a tar from low-temperature carbonization of a sub-bituminous B coal.

- b) Cube-in-air method.

Table II
Structural Parameters of Pitch Fractions

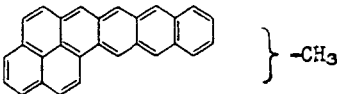
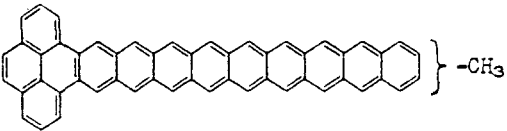
Pitch	2	3	A	5	C	1	6	7	
Pitch Analysis	93.41 4.07	93.31 4.18	93.22 4.24	92.55 4.38	93.29 4.52	93.34 4.36	91.35 4.77 1.11 0.73 2.04	76.94 6.81 0.78 0.29 15.18	
S, % O (diff.), %	2.52	2.51	2.54	3.07	2.19	2.30			
Solvent Fraction*	2	2 + 3	2 + 3	2 + 3	2 + 3	2 + 3	2 + 3	2**	
Analysis of Fraction	92.87 4.34 2.79 1.80 0.040	92.92 4.69 2.42 1.66 0.032	93.09 4.88 2.02 1.65 0.026	92.50 4.91 2.58 1.58 0.033	92.48 4.83 2.68 1.61 0.035	91.80 4.90 3.30 1.57 0.042	92.00 5.18 2.81 1.49 0.034	91.10 5.13 3.61 1.49 0.044	75.84 6.12 18.04 1.04 0.186
Molecular Weight	660	386	350	--	421	459	--	379	455
Yield of Fraction, Wt. %	21.1	65.3	73.6	80.5	70.9	70.9	66.2	83.8	7.4
Hydrogen Distillation	0.946 0.009 0.035 0.010	0.902 0.017 0.064 0.0146	0.892 0.019 0.075 0.0136	0.903 0.016 0.074 0.014	0.890 0.018 0.082 0.011	0.864 0.022 0.098 0.017	0.856 0.025 0.096 0.024	0.802 0.024 0.134 0.042	0.315 -- 0.382 0.303
Structural Parameters	f _a σ Car/Haru	0.987 0.048 1.83	0.974 0.063 1.65	0.972 0.074 1.71	0.971 0.077 1.66	0.963 0.093 1.64	0.958 0.091 1.55	0.943 0.116 1.60	0.670 0.65 1.20

* Solvent Fraction 2 is the carbon-disulfide-soluble, n-hexane-insoluble fraction; Fraction 2 + 3 is the carbon-disulfide-soluble fraction.

** The original Brown-Ladner equations were used to calculate f_a, σ, and Car/Haru for this low-temperature-carbonization pitch fraction.

Table III

Correlation of Structural Parameters in Pitch Fractions
with Possible Type Molecules

PITCH #2 FRACTION or TYPE MOLECULE	PARAMETER VALUES FOR FRACTIONS AND TYPE MOLECULES				
	C/H	Mol. Wt.	fa	σ	Car/Haru
CS ₂ -Soluble Fraction	1.66	386	0.975	0.066	1.71
 (C ₂₈ H ₁₅ -CH ₃)	1.61	364	0.965	0.062	1.75
Resin Fraction	1.80	660	0.987	0.048	1.83
 (C ₅₂ H ₂₇ -CH ₃)	1.77	666	0.981	0.036	1.86

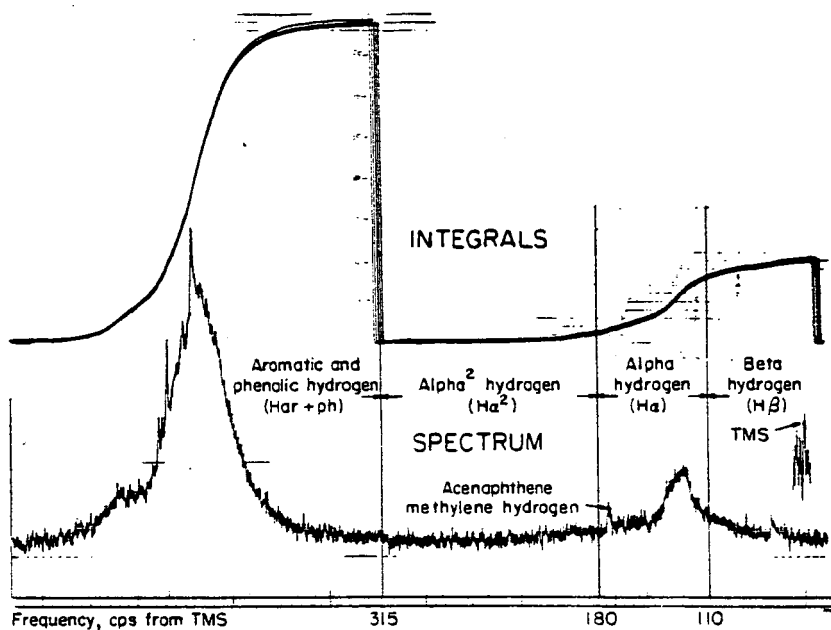


Figure 1. PMR Spectrum and Integrals: Pitch 6, Carbon Disulfide Solubles

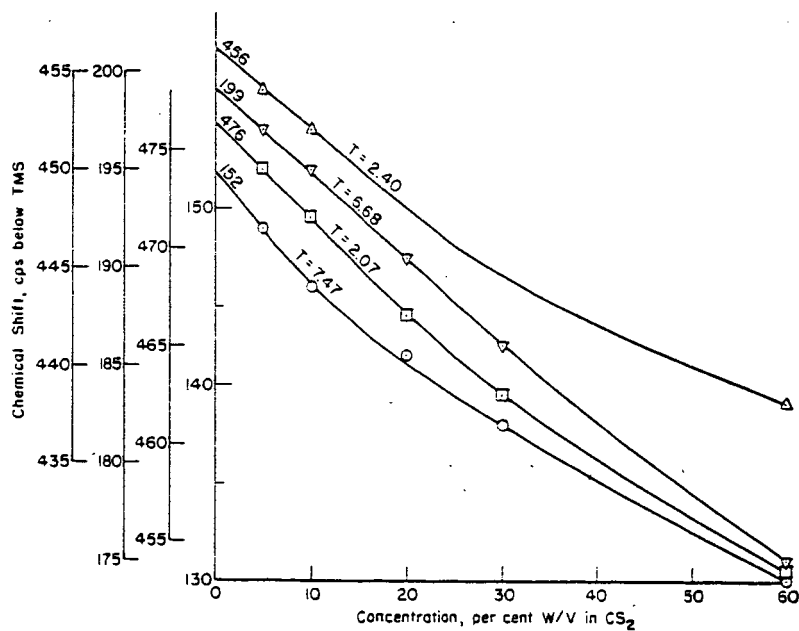


Figure 2. Extrapolation of PMR Frequencies to Infinite Dilution with an Internal Standard: Pitch 1 - CS₂ Extract

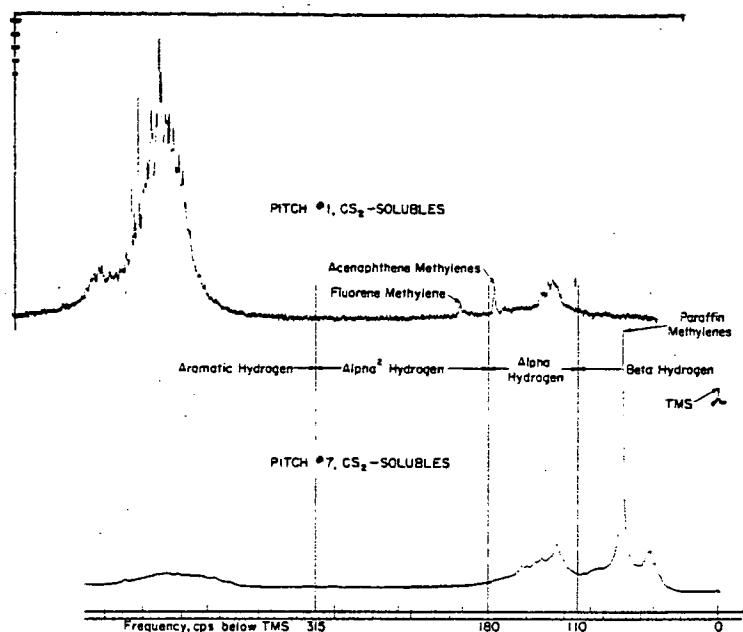


Figure 3. Comparison of PMR Spectra: Coke-Oven Pitch (No. 1) and Low-Temperature-Carbonization Pitch (No. 7); CS₂ Solubles, 60% w/v in CS₂